REPORT DOCUMENTATION PAGE

AFRL-SR-AR-TR-04-

0144

1. AGENCY USE ONLY *(Leave blank)*	2. REPORT DATE	3. REPORT TYPE AND DATES COVERED
	December 15, 2003	Final Technical Report (1 Dec 99 - 30 Sep 03)

4. TITLE AND SUBTITLE	5. FUNDING NUMBERS
High Temperature Strengths and Deformation of Ceramics	F49620-00-1-0082
	2306/BX
	61102F

6. AUTHOR(S)
Sidney Yip

7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES)	8. PERFORMING ORGANIZATION REPORT NUMBER
Massachusetts Institute of Technology Dept of Nuclear Engineering Cambridge, MA 02139-4307	

9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES)	10. SPONSORING/MONITORING AGENCY REPORT NUMBER
AFOSR/NA 4015 Wilson Blvd., Room 713 Arlington, VA 22230-1954 Program Manager: Dr. Joan Fuller	

11. SUPPLEMENTARY NOTES

20040311 063

12a. DISTRIBUTION AVAILABILITY STATEMENT	12b. DISTRIBUTION CODE
APPROVED FOR PUBLIC RELEASE, DISTRIBUTION IS UNLIMITED	

13. ABSTRACT *(Maximum 200 words)*

This project developed a computational modeling capability to study the theoretical strengths and deformation mechanisms of structural ceramics for high temperature applications. The approach adopted was molecular dynamics simulation based on appropriate interatomic potential models. The studies focused on ZrC that has excellent high-temperature properties, and to a lesser extent on SiC and SiO2. Strain-to-failure simulations were performed to observe the details of the structural instability and subsequent microstructural evolution. Besides single crystals, deformations in the amorphous and nanocrystalline phases were also investigated. In parallel elastic stiffness and other mechanical properties were calculated to correlate with and interpret the simulation results. The research performed in this project has demonstrated the feasibility of modeling the intrinsic mechanical and thermal properties of ceramics. The results obtained contribute to a database of structure-property correlation that provides a foundation for further computational studies of ceramics for high temperature applications. It appears that modeling and simulation at the atomistic level have reached a level of physical robustness that one can begin to develop detailed understanding of certain ceramics under conditions of practical interest.

14. SUBJECT TERMS			15. NUMBER OF PAGES
			11
			16. PRICE CODE

17. SECURITY CLASSIFICATION OF REPORT	18. SECURITY CLASSIFICATION OF THIS PAGE	19. SECURITY CLASSIFICATION OF ABSTRACT	20. LIMITATION OF ABSTRACT
U	U	U	

Final Report to the Air Force Office of Scientific Research

Grant Award No. F49620-00-10082

Period: Dec. 1 1999 - Sept. 30, 2003

Program Manager:
Dr. Joan Fuller, Ceramics and Non-Metallic Materials

High Temperature Strengths and Deformation of Ceramics

submitted by

Sidney Yip (Principal Investigator)

Department of Nuclear Engineering
Massachusetts Institute of Technology
Cambridge, MA 02139-4307

Room 24-208 MIT
Ph: (617) 253-3809
Fax: (617) 258-8863
syip@mit.edu

December 15, 2003

1

Contents

A. Summary

The aim of this project was to develop a computational modeling capability to study the theoretical strengths and deformation mechanisms of structural ceramics for high temperature applications. The approach adopted was molecular dynamics simulation based on appropriate interatomic potential models. The studies focused on ZrC which has excellent high-temperature properties, and to a lesser extent on SiC and SiO2. Strain-to-failure simulations were performed to observe the details of the structural instability and subsequent microstructural evolution. Besides single crystals, deformations in the amorphous and nanocrystalline phases were also investigated. In parallel elastic stiffness and other mechanical properties were calculated to correlate with and interpret the simulation results.

The three-year grant was in operation effectively over four years, 2000-2003, as a result of a no-cost extension of 10 months. The major thrusts undertaken during each year were: (Yr. 1) Developed simulation capabilities for strength and deformation studies involving hydrostatic tension and compression loading; began development of an interatomic potential for ZrC. (Yr. 2) Continued ZrC potential development including validation tests; began construction of a model of silica nanorod for tensile failure simulations. (Yr. 3) Performed fracture simulation studies of SiO2 and ZrC using interatomic potentials and shear deformation calculations using first-principles density functional theory codes; continued study of silica nanorod. (Yr. 4) Commenced study of water-silica reaction using quantum chemical techniques

The following studies are considered significant accomplishments of the project.

1. Development and validation of an interatomic potential for ZrC.
2. Theoretical strength of beta-SiC and alpha-SiO_2
3. Uniaxial compression of alpha-quartz
4. Fracture toughness of crystalline quartz
5. Shear response of nanocrystalline ZrC
6. First-principles calculation of affine shear deformation in crystals
7. Shearability gap between ceramics and metals
8. Silica nanorod model for deformation and reaction studies
9. Kinetic pathway for hydrolysis of strained silica nanorod

Each result is discussed further below, followed by a brief section on conclusions and recommendations.

B.   Research Accomplishments

1. Development and Validation of Interatomic Potential for ZrC

The transition metal (refractory) carbide, ZrC, is known for its hardness (Vickers microhardness of 25.5 GPa) and very high melting point (3700K), and high-temperature compressive yield strength. Although brittle at room temperature, it undergoes a brittle-to-ductile transition below 1300K. In order to model its mechanical behavior at the atomistic level, an interatomic interaction model is needed. We have constructed an empirical many-body potential for ZrC with a functional form derived from the formalism of Local Combination of Atomic Orbitals (LCAO), a so-called tight-binding method in electronic structure calculations. The model has 6 parameters in describing the Zr-C bonding, which are fitted to a carefully selected database consisting of cohesive energy curves for three cubic structures, elastic constants of NaCl-ZrC, heat of formation, and most importantly, atomic force constants accurately determined by first-principles density functional theory [1].

To validate our model we systematically calculated the following properties using the potential and compared them with either more rigorous electronic-structure results or experimental measurements – structure and energetics of hexagonal WC phase, carbon vacancy formation and migration energies, metal vacancy formation and migration energies, (001) surface relaxation, bond shrinkage near carbon vacancy, Gruneisen parameter and thermal expansion coefficient, vibrational amplitude and thermal strain, and the melting point. None of these properties were used in fitting the parameters, therefore each comparison serves as an independent test of the robustness of the model description.

We find our potential gives a better description of the various properties than a recent tight-binding model. The reason, we believe, is that the hopping integrals in the latter treatment do not have any angular dependence. Secondly we find the thermal properties of ZrC to be well described by our model. This can be attributed to the fact that the model gives very reasonable phonon dispersion curves when compared against experiments and theoretical calculations. Fundamentally this goes back to our understanding of the nature of bonding in ZrC, namely, a strong bond-angle dependence. The model also gives temperature variations of the thermal strain and vibrational amplitudes in good agreement with measurements. Direct simulation of the melting of a cluster yields 3500K, which can be compared to the experimental value of 3700K.

2. Theoretical Strength of $\beta - SiC$ and $\alpha - SiO_2$

Strength calculations have been performed on $\beta - SiC$ in molecular dynamics simulations using a bond-order potential, a purely covalent description [2]. Cohesive strengths have been determined for single crystal, amorphous, and nanocrystal at room temperature. The single crystal strength, at 38 GPa, represents the upper limit. The amorphous and nanocrystal

values, being close to each other (about 24 GPa), suggest a certain underlying connection between these two types of microstructures. Similar simulations have been extended to $\alpha - SiO_2$ using a potential description consisting of short-range and electrostatic interactions [3]. Under hydrostatic tension we find a polymorphic transition from α to β phase. Since this is a well-known transformation when quartz is heated, we have demonstrated the equivalence between thermal and mechanical strains [4]. Under hydrostatic compression we obtain a transition to amorphous at 20 GPa [5] which is close to the experimental value.

3. Uniaxial Compression of Alpha-Quartz

We have studied alpha-quartz under uniaxial compression with a confining pressure of 1.5 GPa. This mode of loading is chosen to correspond with experiments in geoscience on the longstanding problem of hydrolytic weakening of quartz [6]. In contrast to the response to hydrostatic compression, the lattice deformed elastically up to a critical stress of 14 GPa, and corresponding strain of about 12%, when structural instability set in. Under constant pressure the system deformed in a time-dependent manner on the scale of picoseconds, showing the lattice becoming disordered in a heterogeneous manner of nucleation and growth of a planar region. To our knowledge, this process has not been discussed heretofore. The deformation features revealed by our simulations have correspondence with experimental measurements on plastic deformation of quartz single crystals [7]. The data showed that failure occurred by sudden rupture giving rise to fractures with different orientations and planar structures. We propose that one can distinguish two possible mechanisms for planar fracture - one is the development of shear stresses to activate certain slip systems and give rise to material failure, and the other is the onset of an elastic instability (under compression) to nucleate a local region of disorder which then propagates through the lattice. The former is the conventional view which may be called slip-assisted, and the latter is the one we are presently proposing which may be called instability-assisted [8]. By adopting the instability-assisted mechanism of failure, it is possible to give plausible explanations of several reported observations [7] that are not consistent with the conventional view of slip-based mechanism.

4. Fracture Simulations of Crystalline Quartz

As part of our investigation of strength and deformation, molecular dynamics simulations of crack extension of under mode I (uniaxial tension) loading were performed. Two systems were investigated, an embedded nanocrack and a notch at a free surface [3]. In both simulations the crack extension occurs at a characteristic critical stress, lower in the case of the notch as is expected, in a brittle manner. Contrasting details of strain localization around the crack tip and bond breaking can be seen. The fracture toughness value estimated using the Griffith criterion

compares well experiment, while the value obtained using the Griffith criterion but with an unrelaxed surface energy agrees with the result of direct simulation. This is a demonstration that atomistic simulation and experiment probe quite different time scales of response.

5. Shear Response of Nanocrystalline ZrC

We have deformed several small nanocrystalline samples with grain size varying from 2.4 nm to 5.9 nm by applying a shear stress [3]. We find the shear strength increases with increasing grain size, which is the reverse of the conventional Hall-Petch effect. Previously this behavior has been reported in simulations of nanocrystalline fcc metals; our results indicate that the effect is quite generic, present in ceramics as well as in metals.

6. First Principles Calculations of Affine Shear Deformation in Crystals

Using density functional theory we have shown that aluminum has a higher ideal shear strength than copper, even though the latter has a higher shear modulus [9]. This result is a consequence of the more extended range of deformation before softening in Al, and in turn it can be traced to the directional nature of the chemical binding. By comparing the ion relaxations and valence charge distributions in these two metals, we arrive at contrasting descriptions of bonding characteristics that can explain their relative strength and deformation behavior.

7. Shearability Gap between Ceramics and Metals

We have extended our first-principles calculation of affine shear deformation to a group of fcc and bcc metals and covalent and ionic ceramics [10]. Focusing on the maximum shear strain that a crystal can withstand before yielding, we find spectral gap in the maximum shear strain between ceramics and metals, and a strong correlation of this shearability with the degree of directional bonding. Furthermore we show that incorporating shearability as a material parameter one can capture quantitatively the stress-strain behavior of perfect metallic and ceramic crystals, thus putting our fundamental understanding of shear deformation on the same footing with the universal description of tensile cohesion in solids. Together these constitutive relations allow useful materials design and performance criteria to be formulated where shear and tensile deformation modes compete.

8. Model of Silica Nanorod for Deformation and Reaction Studies

Current interest in nanoscience and technology has stimulated an awareness that mechanical behavior in small dimensions can have significant deviations from properties normally associated with structures at the two extremes, an isolated cluster of atoms or a macroscopic specimen. Unlike physical properties which deviate from continuum behavior only on the atomic scale, mechanical strength and deformation are controlled by defects in the assembly which in themselves can range from angstrom to nanometer to micometer length scales. We have introduced a nanorod as a novel, stand-alone system which has advantages over a cluster in that meaningful mechanical behavior can be extracted and scale up continuously to larger

6

dimensions. The rod is also more suitable than a bulk system for the study of stress and chemical reaction because one has better control over the atomic site for structural defect nucleation or chemical bond reaction. We analyzed mechanical response of a 144-atom nanorod of SiO2 in uniaxial tension and compression and compared the results to in-house simulations of bulk quartz [11]. This work is a prelude to the study of the effects of water on the mechanical strength of silica, which is a fundamental issue in understanding the dislocation mechanism of hydrolytic weakening [6].

9. Kinetic Pathway for Hydrolysis of Strained Silica Nanorod

We are currently investigating a particular problem of environmental effect on the mechanical strength of a ceramic material, that of hydrolytic weakening and stress corrosion of silica. We are interested in the kinetics of hydrolyzing the strained Si-O bond, the microscopic mechanism, the reaction pathways and rate. That the presence of water has a significant effect on strength of quartz, particularly at high temperature, is well known. It has been proposed that the fundamental mechanism for this effect is the hydrolysis of a siloxane bond, which bridges two neighboring SiO_4 tetrahedra, to form two terminal silanol groups [6]. The silanol groups in turn will facilitate bond rupture and thus lower the strength of silica. Since the problem involves bond breaking and formation, and significant effects of charge transfer, classical potential simulations will not be adequate. To keep the system to a size that permits quantum calculations, we are studying the nanorod which we have recently developed. Initially we are applying a semi-empirical molecular orbital method as implemented in a general-purpose package MOPAC. Our preliminary results on sampling the reaction pathways indicate a three-step mechanism for the hydrolysis -- adsorption of the water molecule, water reaction with the siloxane bond Si-O-Si involveing dissociation and proton transfer, and formation of silanol group SiOH [12]. Knowing the pathways we are able to determine the activation barrier and study its variation with strain on the nanorod.

References Cited

[1]   J. Li, D. Liao, S. Yip, R. Najafabadi, L. Ecker, "A Force-Based Many-Body Interatomic Potential for ZrC", J. Appl. Phys **93**, 9072 (2003).

[2]   J. Li and S. Yip, "Atomistic Measures of Materials Strength", Computer Modelling in Engineering and Sciences **3**, 219 (2002)

[3] D. Liao, "Atomistic Simulation of Strength and Deformation of Ceramic Materials", Ph.D. Thesis, MIT, August 2001.

[4] D. Liao, "Transitions of Quartz Under External Loadings", to be submitted.

[5] S. Subramanian, S. Yip, "Structural Instability of Uniaxially Compressed Alpha-Quartz", Comp. Mater. Sci. **23**, 116 (2002).

[6] D. T. Griggs, "Hydrolytic Weakening of Quartz and Other Silicates", Geophys. J. R. Astron. Soc. **14**, 19 (1967).

[7] J. M. Christie, H. C. Heard, P. N. LaMori, Am. J. Sci. **262**, 26 (1964).

[8] S. Subramanian, "Atomic-Level Deformation Response of SiO_2 under Compression", MS Thesis, MIT, May 2001.

[9] S. Ogata, J. Li, S. Yip, "Ideal Pure Shear Strength of Aluminum and Copper", Science **298**, 807 (2002).

[10] S. Ogata, J. Li, N. Hirosaki, Y. Shibutani, S. Yip, "Shearability Gap between Metallic and Covalent Bonding", Phys. Rev. Lett., submitted.

[11] T. Zhu, J. Li, S. Yip, R. Bartlett, S. B. Trickey, N. H. de Leeuw, "Deformation and Fracture of a SiO_2 Nanorod", Molecular Simulations **29**, 671 (2003).

[12] T. Zhu, J. Li, X. Lin, S. Yip, "Atomistic Measures of Deformation and Reaction Dynamics: Defect Nucleation Criterion and strain-Dependent Reactivity", invited talk presented at MRS Boston, Dec. 1-5, 2003, Symposium AA: Synthesis, Characterization, and Properties of Energetic/Reactive Nanomaterials.

C. Conclusions and Recommendations

The research performed in this project has demonstrated the feasibility of modeling the intrinsic mechanical and thermal properties of ceramics. The results obtained contribute to a database of structure-property correlation which provides a foundation for further computational studies of ceramics for high temperature applications. It appears that modeling and simulation at the atomistic level have reached a level of physical robustness that one can begin to develop detailed understanding of certain cramics under conditions of practical interest, such as in high-temperature and reactive environments in synthesis and performance.

Discussions at the recent Ultra High Temperature Ceramics Program Review, Wintergreen, VA, November 5-7, 2003, have focused on a number of issues pertaining to the synethesis, structural evolution, and characterization of mechanical and thermal properties of diborides and carbides. Specifically there is a need for a more fundamental understanding of strength retention at high temperature, mechanisms of oxidation, and combustibility at high

8

oxygen pressure. It is our belief that quantum chemical calculations combined with atomistic simulations of the kind described here provides a capability to achieve the physical understanding and insights that can help to interpret existing experimental data, as well as guide further efforts in synthesis and materials development.

D. Publications

The following publications report work supported wholly or in part by the Grant.

S. Yip, J. Li, M. Tang, J. Wang, "Mechanistic Aspects and Atomic-Level Consequences of Elastic Instabilities in Homogeneous Crystals", Materials Science and Engineering A**371**, 236 (2001).

J. Li, W. Cai, J. Chang, S. Yip, "Commentary on Atomistic Simulations of Materials Strength and Deformation: Prospects for Mechanistic Insights", *in Materials Science for*
the 21st Century, Society of Materials Science, Japan, 2001, vol. A, p. 220-233.

M. de Koning, A. Antonelli, S. Yip, "Single-Simulation Determination of Phase Boundaries: A Dynamic Clausius-Clapeyron Integration Method", J. Chem. Phys. **115**, 11025 (2001).

S. Yip, J. Li, M. Tang, J. Wang, "Mechanistic Aspects and Atomic-Level Consequences of Elastic Instabilities in Homogeneous Crystals", Materials Science and Engineering A**371**, 236 (2001).

J. Li, W. Cai, J. Chang, S. Yip, "Commentary on Atomistic Simulations of Materials Strength and Deformation: Prospects for Mechanistic Insights", *in Materials Science for the 21st Century*, Society of Materials Science, Japan, 2001, vol. A, p. 220-233.

M. de Koning, A. Antonelli, S. Yip, "Single-Simulation Determination of Phase Boundaries: A Dynamic Clausius-Clapeyron Integration Method", J. Chem. Phys. **115**, 11025 (2001).

S. Subramanian, "Atomic-Level Deformation Response of SiO_2 under Compression", MS Thesis, MIT, May 2001.

D. Liao, "Atomistic Simulation of Strength and Deformation of Ceramic Materials", Ph.D. Thesis, MIT, August 2001.

A. Romano, J. Li, S. Yip, "Atomistic Simulation of Matter Under Stress: Crossover from Hard to Soft Materials", Physica A **304**, 11 (2002).

J. Li and S. Yip, "Atomistic Measures of Materials Strength", Computer Modelling in Engineering and Sciences **3**, 219 (2002)

S. Subramanian, S. Yip, "Structural Instability of Uniaxially Compressed Alpha Quartz", Computational Materials Science **23**, 116 (2002).

J. Li, K. J. Van Vliet, T. Zhu, S. Suresh, S. Yip, "Atomistic Mechanisms Governing Elastic Limit and Incipient Plasticity in Crystals", Nature **418**, 307 (2002).

S. Ogata, J. Li, S. Yip, "Ideal Pure Shear Strength of Aluminum and Copper", Science **298**, 807 (2002).

S. Yip, "Synergistic Science", Nature Materials **2**, 3 (2003).

K. J. Van Vliet, J. Li, T. Zhu, S. Yip, S. Suresh, "Quantifying the Early Stages of Plasticity through Nanoscale Experiments and Simulations", Phys. Rev. B **67**, 104105 (2003).

J. Li, D. Liao, S. Yip, R. Najafabadi, L. Ecker, "A Force-Based Many-Body Interatomic Potential for ZrC", J. Appl. Phys **93**, 9072 (2003).

W. Cai, V. V. Bulatov, J. Chang, J. Li, S. Yip, "Periodic Image Effects in Dislocation Modelling", Philos. Mag. A **83**, 539 (2003).

T. Zhu, J. Li, S. Yip, R. Bartlett, S. B. Trickey and N. de Leeuw, "Deformation and fracture of a SiO2 nanorod", Molecular Simulation **29**, 671-6 ((2003).

N. de Leeuw, Z. Du, J. Li, S. Yip, T. Zhu, "A Computer Modelling Study of the Effect of Hydration on the Stability of a Silica Nano-tube", Nano Lett. **3**, 1347 (2003).

T. Zhu, J. Li, K. J. Van Vliet, S. Suresh, S. Ogata, S. Yip, "Predictive Modeling of Nanoidentation-Induced Homogeneous Nucleation of Dislocation in Copper", J. Mech. Phys Solids (in press).

J. Li, T. Zhu, S. Yip, K. Van Vliet, S. Suresh, "Elastic Criterion for Dislocation Nucleation", Mat. Sci. & Eng. (in press).

S. Ogata, J. Li, N. Hirosaki, Y. Shibutani, S. Yip, "Shearability Gap between Metallic and Covalent Bonding", Phys. Rev. Lett., submitted.

S. Subramanian, D. Liao, S. Yip, "Structural Instability in Uniaxially Compressed α-Quartz: An Anisotropic Failure Mechanism", to be submitted to Physical Review B.

D. Liao and S. Yip, "Molecular Dynamics of $\alpha - \beta$ Transition in Quartz: Pseudo-critical Behavior, Soft Mode, and the Inhomogeneous Phase", to be submitted to Journal of Chemical Physics.

E. Personnel

Besides the Principal Investigator, Sidney Yip, the project has supported Mr. Dongyi Liao, a graduate student in Nuclear Engineering as a Research Assistant, until his graduation in August, 2001, and Mr. Ting Zhu, a graduate student in Mechanical Engineering, since the summer of 2001. In addition, Dr. Ju Li, previously a postdoctoral fellow at MIT and now Assistant Professor of Materials Science and Engineering at Ohio State University, Professor Shigenobu Ogata in the Department of Mechanical Engineering at Osaka University (Japan), and

Mr. Sundararaman Subramanian, a graduate student in Nuclear Engineering until his graduation in May 2001, participated actively in the research.